Branched Carboxylic Acids from Long-Chain Unsaturated Compounds and Carbon Monoxide at Atmospheric Pressure¹

Carbon monoxide at atmospheric pressure adds readily to the double bonds of certain long-chain unsaturated compounds in concentrated sulfuric acid to produce branched carboxylic acids. Unsaturated compounds studied were oleic acid, 10-hendecenoic acid, oleyl alcohol, methyl ricinoleate, and linoleic acid. A major component from the reactions of the last two compounds is the same.

Infrared spectrophotometry and gas-liquid chromatography have been the major tools employed in determining composition and structure of the products in addition to the usual chemical and physical determinations.

Both the concentration and quantity of sulfuric acid are critically important variables in determining the yields. Water is an essential reactant also and must be available throughout the reaction

Carbon monoxide has been prepared and utilized in situ by a modification of Koch's (1) method in which the unsaturated compound mixed with formic acid is added to concentrated sulfuric acid or carbon monoxide from a cylinder is passed through sulfuric acid to which the unsaturated compound is added. A method for preparing methyl and butyl esters of carboxyl groups which are difficult to esterify is described.

Reaction mechanisms involving intermediate carbonium and oxocarbonium ions are proposed to account for the products.

DICARBOXYLIC ACIDS are important intermediates in the preparation of polymers, plasticizers, lubricants, and other functional fluids. At the present time the only commercial methods of preparation of dicarboxylic acids from fat sources are cleavage methods. The most important of these are ozonolysis and alkaline fusion although in the recent past chromic acid oxidation has also been employed.

One of the inherent drawbacks to a cleavage method is that it may not be sufficiently selective in its point of attack, thereby producing not just two but many products. Aside from the obvious difficulties in cleanly separating complex mixtures on a commercial scale, there is the ever-present problem that all of the cleavage products are not equally valuable and are salable only at unprofitable price levels, if at all. This is self-defeating from the fat-utilization standpoint inasmuch as dicarboxylic acids from nonfat sources are relatively low-priced substances and those prepared from fats must also be low cost to compete effectively.

An approach to which we have been giving considerable thought and attention is one in which the entire fatty molecule is employed. This demands that a) a group be introduced which is readily converted to the carboxyl group (the nitrile group is one example), or b) a direct carboxylation technique be utilized.

It has been known for some time that carbon monoxide under high pressure in the presence of the Lewis type of catalysts can be used for the direct carboxylation of alkenes and unsaturated fatty materials. The necessity for the use of high pressure and the relatively modest yields are discouraging features to such work. Our interest in carboxylation with carbon monoxide was revived by the interesting reports of Koch and Haaf (1), who showed that a wide variety of unsaturated compounds could be directly carboxylated with carbon monoxide and water at atmospheric or only moderate pressures in the presence of concentrated sulfuric acid, as solvent and reaction medium, a system with which we had worked extensively (2). Although Koch studied numerous alkenes, only two long-chain unsaturated fatty compounds were reported, namely, undecylenic and oleic acids. With the former, carboxylation was reported to give two C₁₂ dicarboxylic acids, and limited characterizing data were supplied. With oleic acid, no characteristics of the products were given. The only statement concerning the reaction of oleic acid with carbon monoxide and water in the presence of concentrated sulfuric acid was that a C₁₉ dicarboxylic acid was formed in good yield.

In this paper is described the direct carboxylation at atmospheric pressure of some unsaturated fatty acids, esters, and alcohols in concentrated sulfuric acid with either gaseous (cylinder) carbon monoxide or by an in situ method which is a modification of that described by Koch, in which formic acid is decomposed to carbon monoxide and water by the concentrated sulfuric acid while the unsaturated component is being added. As shown later in the experimental part, to obtain high carboxylation yields it is necessary to employ ratios of formic acid and sulfuric acid to double bond which are considerably different from those recommended (1). In a formal sense, as illustrated with oleic acid, the molecules of carbon monoxide and water add across a double bond to introduce a carboxyl group as a branch in the chain:

¹ Presented at the annual meeting, American Oil Chemists' Society, Dallas, Tex., April 4-6, 1960.

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In addition, we have isolated the reaction products, characterized them by chemical and physical methods, and prepared esters from them. The role of water in obtaining high yields of carboxylated products has also been examined. The infrared spectra of the products have been obtained as an aid in the proof of their structure, and these are also reported. In certain cases gas-liquid chromatography (GLC) has been utilized to indicate that a number of isomers are formed.

Experimental

Starting Materials. Oleic acid (93%) was prepared from commercial oleic acid by one low-temperature crystallization and fractional distillation. Highly purified (98–99%) oleyl alcohol (3), methyl ricinoleate (4), linoleic acid (5), and 10-hendecenoic acid (6) were prepared by described procedures.

Preparation of Branched-Chain Carboxylic Acids. Gaseous Carbon Monoxide Method. Carbon monoxide was passed through 80.4 g. (0.795 mole) of 97.2% sulfuric acid contained in a 500-ml., three-neck flask, using a gas dispersion tube with a coarse fritted cylinder. With stirring 7.1 g. (0.025 mole) of oleic acid were added drop by drop in 16 min. to the sulfuric acid solution, which was saturated with carbon monoxide. Carbon monoxide was allowed to pass through the stirred mixture for a total of 2 hrs. while the temperature was maintained between 9 and 13° with external cooling. At the end of this time the mixture was poured into approximately 300 ml. of a mixture of ice and water. The product was extracted with ether and washed free of sulfuric acid. The ether solution was dried over anhydrous sodium sulfate and filtered; the ether was then evaporated, yielding 6.4 g. of pale yellow syrupy material with an iodine number of 12.9, acid number, 300, and saponification

Preparation of Branched-Chain Carboxylic Acids. Formic Acid Method. A mixture of 28.3 g. (0.1 mole) of oleic acid and 23.5 g. (0.5 mole) of 98% formic acid in a cylindrical dropping funnel was stirred vigorously and added in 35 min. to 242.2 g. (2.4 moles) of 97.2% sulfuric acid with rapid stirring. A 5-liter flask was used because of copious foaming. The temperature was maintained between 10 and 20° by external cooling. After the reactants were mixed, stirring was continued for an additional 2 hrs. and 25 min. for a total reaction time of 3 hrs. At the end of this time the mixture was poured into approximately 1 liter of a mixture of ice and water and worked up as described above. A yield of 29.8 g. of pale yellow syrupy material was obtained with an iodine number of 2.3, acid number, 297, and saponification number, 305.

The reaction product (27.9 g.) was distilled from an alembic flask. Four fractions were taken, two of which were predominantly dicarboxylic acids and were light yellow viscous liquids. One of these fractions b.p. 199–200° (0.45 mm.) weighed 14.5 g. (acid number 325); the other, b.p. 200–201° (0.45 mm.) weighed 3.7 g. (acid number 341). Anal. calcd. for carboxystearic acid, $C_{19}H_{36}O_4$: C, 69.5; H, 11.1; acid number, 342; molar refractivity, 93.5. Found: (latter fraction) C, 69.4; H, 11.7; molar refractivity, 92.8.

The fraction with an acid number of 325, consisting mainly of carboxystearic acid, was converted to methyl esters by refluxing 13.8 g. with 68 ml. of

anhydrous methanol and 5.3 g. (3.9 ml.) of dimethyl sulfate for 42 hrs. The product was worked up by neutralizing the dimethyl sulfate with aqueous sodium carbonate solution in the cold and extracting with ether. (In larger preparations, from one-half to two-thirds of the alcohol was distilled off before neutralization and dilution.) Distillation of 9.4 g. of the methyl esters from an alembic flask yielded 5.8 g. of a clear, mobile amber liquid, b.p. 146–148° (0.35 mm.), $n^{30/D}$ 1.4465. Anal. calcd. for $C_{21}H_{40}O_4$: C, 70.7; H, 11.3; molar refractivity, 102.8. Found: C, 70.6; H, 11.3; molar refractivity, 102.6.

The method just described was used in the carboxylation of oleyl alcohol, methyl ricinoleate, and 10-hendecenoic acid. With linoleic acid the quantities of formic acid and sulfuric acid were doubled; otherwise the procedure was the same. After pouring the reaction product obtained by carboxylation of oleyl alcohol into an ice and water mixture, it was necessary to hydrolyze the sulfate ester by boiling. After this the product was worked up as described. In all of the preparations, except the one experiment described above, the crude reaction products were converted directly to methyl esters before distilling.

The dibutyl ester of carboxystearic acid was prepared either by direct esterification or by ester interchange from the dimethyl ester. In direct esterification it was necessary to elevate the boiling point in order to obtain complete reaction. Cymene was used for this purpose, but it made the recovery of the product difficult.

The ester-interchange reaction was carried out in the following way. To 33.5 g. of methyl esters (acid number 6.3) prepared from crude carboxystearic acid (acid number 310) were added 142 ml. of n-butanol with which 0.42 g. of metallic sodium had been reacted, and the mixture was refluxed for 25 hrs. To determine when the interchange was complete, the methanol evolved was removed and measured. For this purpose a 1 x 20-in. fractionating column packed with Raschig rings was used. The product was worked up by pouring the reaction mixture into dilute hydrochloric acid and extracting with ether. After washing the ether layer free of acid, it was dried over sodium sulfate and filtered; the ether was then evaporated, yielding 40.9 g. of crude dibutyl esters with an acid number of 10.7. The acidity of the crude dibutyl esters was neutralized with potassium hydroxide, and the product was vacuum-distilled.

The distilled dibutyl esters of carboxystearic acid obtained by the two methods of preparation had the same properties (Table IV).

Infrared Spectra. Infrared spectra were obtained on a Perkin Elmer Model 21 double beam recording spectrophotometer. For general spectra a demountable cell consisting of sodium chloride windows (one window with a moat-type channel) (7), and 0.025 and 0.03 mm. spacers was used since all samples were liquid. Where dilution studies were made, reference to this is made in the text; these spectra were determined with a 0.2-mm. cell.

Gas-Liquid Chromatography (GLC). Conventional type of GLC equipment was employed. A four-filament, thermal conductivity cell, and 2-millivolt, 114 in. strip-chart recorder requiring 2 seconds for full-scale pen deflection was used. The column, 8 ft. long by $\frac{3}{16}$ in. O.D. and $\frac{1}{8}$ in. I.D., was of stainless steel

and packed with 10.1 g. of 60-80 mesh, acid-washed Chromosorb coated with 1.5 g. (15%) of a succinate-adipate diethylene glycol polyester. The column was operated at 230°, and a flow rate of 30 ml. of helium per minute was maintained at the column exit. The sample used was approximately 0.2 mg.

Results and Discussion

Reaction Conditions. An important variable in the high-yield atmospheric carboxylation of unsaturated compounds, which has not been described by Koch (1), is the concentration and quantity of water. The importance of water is quite evident and is shown in Table I. In all of these experiments the amount of water does not change during carboxylation since the carbon monoxide is generated externally.

TABLE I
Reaction of Oleic Acid with Gaseous Carbon Monoxide

Expt. number		Mole ratio)	Sulfuric	Time,	Acid	Iodine number	
	Oleic acid	Sulfuric acid	Watera	acid, %	hrs.	numberb		
1	1	5.5	3.0	91	2	150°	18	
2	1	9.6	1.5	97	2	222	••••	
3	1	9.6	1.5	97	6	226		
4	1	18.0	2.8	97	1	252	34	
5	1	19.1	3.0	97	2	287	20	
6	1	31.8	5.0	97	2	300	13	
7	1	63.6	10.0	97	2	297	16	
. 8	1	24.0	0	100	2	2154	63	

^a Water present in sulfuric acid.
^b Saponification number essentially the same as acid number except where given below.

here given below.

^c Saponification number 201.

^d Saponification number 251.

With 91% sulfuric acid (Expt. 1) no carboxylation takes place. The sulfuric acid is too dilute since the same amount of water in more concentrated sulfuric acid (Expt. 5) is adequate. On the other hand, 1.5 moles of water is insufficient for carboxylation to proceed beyond a limited extent (Expt. 2) even though the concentration of sulfuric acid is 97%. The greatest increase in acid number and decrease in iodine number, indicating maximum carboxylation, is obtained when five moles of water per mole of oleic acid is employed (Expt. 6). With 100% sulfuric acid (Expt. 8) little, if any, carboxylation is evident, which shows conclusively that water must be present during the reaction. Increasing the amount of water above five moles per mole of oleic acid (Expt. 7) or increasing the reaction time beyond two hours does not increase the amount of carboxylation.

In Table II are shown the results obtained by the reaction of oleic acid with carbon monoxide and water using the formic acid decomposition method. To maintain a high concentration of sulfuric acid

TABLE 11
Reaction of Oleic Acid with Carbon Monoxide from Formic Acid

Expt. number Oleic Formic acid acid		Mole rati	0		furic 1, %	m.		7 11
	Sul- furic acid	Start	Finish	Time, hrs.	Acid number	Iodine number		
1	1	1.1	6 8	100	96.6	2 2 3 6 6	205	37
1 2 3 4 5	1 1	2 5 2 3	24	100 100	$95.4 \\ 96.1$	2	218 293	26 28
4	i	2	24	97	95.5	6	289	20
5	ī	3	24	97	94.8	6	315	8
6	1	5	24	97	93.6	2	296	5
	1 1 1	5 5 5	$\bf 24$	97		2 3 6	306	••••
	1	. 5	24	97	•••••	6	310 a	6
7	1	5	48	97	94.9	3 6	316	5 5
8	1	9	24	97	90.6	6	308	5

a Highest value obtained in duplicate runs was 323 (calcd. 342).

in these experiments it is necessary to use a high mole ratio of sulfuric acid to oleic acid to take care of the water formed by the decomposition of formic acid. No advantage in starting with 100% sulfuric acid is indicated (Expt. 1, 2, 3). Actually the results are not as good as with 97% sulfuric acid (Expt. 4–8), and with 100% sulfuric acid there is some undesirable decomposition as shown by charring. These results indicate the need for an excess of water at all times, a conclusion previously reached from the results in Table I.

Effect of the variable time is shown in Experiment 6, Table II. Three hours of reaction time give slightly more carboxylation than do two hours, as shown by the increase in acid number from 296 to 306. The increase to 310 in 6 hrs. however is not considered significant. The greatest amount of carboxylation (Expt. 5, 6, 7), as shown by the increase in acid number and the decrease in iodine number, is obtained when three to five moles of formic acid per mole of oleic acid are used with a sufficient quantity of concentrated sulfuric acid to maintain a final concentration of from about 93 to 95%. Experiments 7 and 8 show that further increase in the excess of formic acid or sulfuric acid over the quantities used in Experiment 6 is unnecessary.

Because of the slightly higher carboxylation obtained with the formic acid decomposition method, this method was used for the remaining preparative work. Table III shows the high recovery of crude reaction products and the extent to which they are carboxylated by comparing the acid number of the product with that calculated. The reduction in iodine number from that of the starting material also indicates the extent of the reaction. The saponification number of the products obtained from oleic acid, 10-hendecenoic acid, and oleyl alcohol are essentially

TABLE III
Characteristics of Crude Reaction Products

Oligiaciónsico di Oligia Doución i l'occordi											
	Yield,a	Acid No.		Sapon. No.		Iodine No.		% Hydroxyl			
Starting material	g.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
Oleic acid	32 33 29	342 487 178 157 344	297 446 135 217 ^b 275 ^c	342 487 178 313 344	305 450 138 319 306	0 0 0 0 78	2 5 5 19 48	5.4 4.7	 4.8 1.4		

a Yield based on 30 g. of starting material.

CH₃(CH₂)₅CH—(CH₂)_x—CH—(CH₂)_yCOOCH₃ OH COOH

(x+y=9)

High acid number is probably caused by partial hydrolysis of methyl group.

(x + y = 9)

Calculated values are for: $CH_3(CH_2)_4CH = CH(CH_2)_x - CH - (CH_2)_y - COOH$ COOH(x

b Calculated values are for:

Compound	Boiling point		Carbon, %		Hydrogen, %		n ^{30/D}	d30	Molecular refraction	
	°C.	mm.	Calcd.	Found	Calcd.	Found			Calcd.	Found
Carboxystearic acid Dimethyl ester of carboxystearic acid Dibutyl ester of carboxystearic acid Dimethyl ester of carboxyhendecanoic acid Methyl ester of carboxyoctadecanol Methyl ester of carboxylated methyl ricinoleate a Methyl ester of carboxylated linoleic acid a	$\begin{array}{c} 200-201\\ 146-148\\ 183-185\\ 93-94\\ 153-155\\ 161-162\\ 160-161\\ \end{array}$	0.45 0.35 0.40 0.35 0.45 0.40 0.40	69.5 70.7 73.6 65.1 73.1 70.6 70.6	69.4 70.6 73.4 65.2 73.0 69.2 68.7	11.1 11.3 11.6 10.1 12.3 10.7 10.7	11.7 11.3 11.8 10.3 12.3 10.7 10.7	1.4615 1.4465 1.4465 1.4373 1.4535 1.4530 1.4530	$\begin{array}{c} 0.9726 \\ 0.9281 \\ 0.9033 \\ 0.9684 \\ 0.9095 \\ 0.9628 \\ 0.9699 \end{array}$	93.5 102.8 130.6 70.2 98.0 96.0 96.0	92.8 102.6 130.1 69.9 97.7 95.6 94.9

a % C, % H, and molecular refraction calculated for CH3(CH2)5CH-(CH2)x-CH-(CH2)yCOOCH3

(x + y = 9; x probably = 1 or 2)

the same as the acid number; with methyl ricinoleate and linoleic acid however the saponification number is quite different from the acid number. This suggests that an ester or lactone has formed in the latter two cases. Also the hydroxyl value of the product obtained from methyl ricinoleate is much lower than would be expected. The significance of these points will be discussed later in more detail. The hydroxyl value for the product obtained from oleyl alcohol is slightly lower than that calculated for one hydroxyl group. This is thought to result in part from the errors of the method. Koch (1) reported that alcohols can also be carboxylated; however in this case the slightly lower value does not appear to be due to replacement of the hydroxyl group by carboxyl since under identical conditions 1-dodecanol is not carboxylated and is recovered essentially unchanged.

Carboxystearic Acid. The product obtained by the carboxylation of oleic acid is a pale yellow viscous liquid, which could not be purified by low-temperature solvent crystallization; it distills readily however at about 200° and 0.45 mm. to give a product having the calculated acid number, carbon and hydrogen and molecular refraction (Table IV).

The usual method of direct esterification does not completely esterify the branched carboxyl group. Using dimethyl sulfate (see Experimental), nearly complete esterification is obtained after 42 hrs. of reflux. Esterification of other branched-chain carboxylic acids which were prepared also takes a long time. The long time required for complete esterification provides chemical evidence for a branched carboxyl group as it is well known that such structures behave in this way.

The dimethyl esters of carboxystearic acid distill at 146–148° at 0.35 mm. as a colorless mobile liquid with the correct chemical and physical properties (Table IV). Gas-liquid chromatographic analysis of the heart cut shows four or five closely related major components. Together with the information from the infrared spectra and chemical analyses it is concluded that these components are isomers. The formation of isomers is to be expected from a reaction conducted in concentrated sulfuric acid in which carbonium ion intermediates are probable (see later discussion).

The dibutyl esters of carboxystearic acid can also be prepared by direct acid catalyzed esterification with butanol, using cymene to raise the boiling point. A more satisfactory method however is ester interchange because of the shorter reaction time and the ease of handling. Both the methyl and butyl esters cannot be completely hydrolyzed by refluxing with dilute alcoholic potassium hydroxide in 8 hrs. This

is additional chemical confirmation of a branched carboxylic ester group. Table IV also summarizes the characteristics of the dibutyl esters.

Carboxyhendecanoic Acid. The product obtained by carboxylation of 10-hendecenoic acid is a pale yellow viscous liquid. Two possible isomers are immediately apparent and have been described by Koch (1), one in which the carboxyl group is attached as a branch to the penultimate carbon atom and the other in which the carboxyl group is attached to the terminal carbon atom giving an a,ω -dicarboxylic acid. The latter, 1,10-decanedicarboxylic acid, is known (8) and is a high-melting crystalline solid. Low-temperature solvent crystallization of carboxylated 10-hendecenoic acid fails to separate any solid material and, as will be shown later, the spectrum indicates that 1,10-decanedicarboxylic acid cannot be present in large amount, if at all.

Gas-liquid chromatographic separations of the dimethyl esters of the reaction product, as well as on a heart cut of the distilled methyl esters, are much the same and show the presence of three closely related major components, which are undoubtedly isomers. The relative amounts of the three major components in the distilled products are 6, 23, and 71%. It is concluded that about 94% of carboxylated hendecenoic acid is branched and not more than 6%, if any, can be $a_{,0}$ -dicarboxylic acid.

Infrared spectra as well as chemical and physical data confirm that the product is the dimethyl ester of carboxyhendecanoic acids (Table IV).

Carboxyoctadecanol. A branched-chain monocarboxylic acid is obtained by the carboxylation of oleyl alcohol. Distillation of the methyl ester of carboxyoctadecanol yields several fractions with the index of refraction at 30° ranging from 1.4510 to 1.4540 (Table IV). The infrared spectra of these fractions are essentially identical and have all of the characteristic features of the expected compound, as will be shown later. This is typical of the preparations already discussed and of those to follow. It is apparent that shifting of the carbonium ion along the chain of the molecule occurs, resulting in the formation of isomers.

Carboxylated Methyl Ricinoleate. The apparent anomaly shown in Tables III and IV in respect to the structure of the product obtained by carboxylation of methyl ricinoleate is explained by the fact that both structures are present in the crude reaction product; the lactone appears as a minor constituent but becomes enriched in the distillate.

As has already been pointed out with oleyl alcohol and 1-dodecanol, there is little or no evidence for

replacement of the hydroxyl group by carboxyl. The acid and saponification numbers of the reaction product from methyl ricinoleate are not sufficiently high to suggest that the hydroxyl group has been replaced by carboxyl. This is confirmed by the infrared spectrum of the methyl esters of the product in that the absorption is not sufficiently great to account for the introduction of two branched carboxyl groups. The low hydroxyl value in the crude product is best accounted for by a lactone structure.

Distillation of the methyl esters yields a product with no hydroxyl. The infrared spectra of both the undistilled and distilled products show an absorption in the 1765 cm. region which suggests the presence of a lactone. This will be discussed more fully under infrared spectra. Carbon, hydrogen, and molecular refraction most nearly fit such a structure (Table IV) although it is not yet possible to be certain of the size or exact position of the lactone ring. Other structures, such as anhydrides, ethers, and phorones, have been considered, but these structures do not fit the chemical and infrared data.

Carboxylated Linoleic Acid. Carboxylation of linoleic acid might be expected to give a dicarboxylic or tricarboxylic acid, depending on whether one or both unsaturated centers are attacked. The chemical data in Table III show that tricarboxylic acid is a minor product, if present at all. The infrared spectra of the distilled methyl esters of the reaction product bear this out in that the expected absorption is not sufficiently intense to account for the introduction of two branched carboxyl groups.

The unsaturation still present in the crude carboxylated linoleic acid is not due to unreacted linoleic acid, as shown by alkaline isomerization. The ultraviolet absorption spectrum of the isomerized and unisomerized samples are the same. The unsaturation therefore must be in an unsaturated dicarboxylic acid.

A comparison of the chemical and physical data obtained on the distilled methyl esters of carboxylated linoleic acid with those of the distilled methyl esters of carboxylated methyl ricinoleate (Table IV) shows a close similarity. The infrared spectra of the two products are essentially identical. The inevitable conclusion is that the methyl esters of carboxylated methyl ricinoleate and of linoleic acid are identical. A suggested reaction path to account for lactone formation in the carboxylation of linoleic acid is that one double bond is carboxylated and that this carboxyl group, which is favorably located sterically, then adds to the remaining double bond.

Infrared Spectra. The structural similarity among the methyl esters of the carboxylated products is strikingly apparent when the spectra are closely compared. The spectrum of the dimethyl esters of carboxyhendecanoic acids (Figure 1, A) is decidedly different from that of a, w-dimethyl esters of dicarboxylic acids, thus showing that terminal carboxylation is a minor reaction if it occurs at all. The spectrum shows a weak band at 1350 cm.-1, indicating the presence of a branched hydrocarbon chain. Such a band is missing in the esters of normal fatty acids and of a,ω-diacids. A band at 1380 cm.-1 indicates the presence of a C-CH₃ grouping. As expected, the spectrum of the dimethyl esters of carboxystearic acid (Figure 1, B) shows the general features of methyl esters, but a shoulder in the 1350 cm.-1 region indicates a branched hydrocarbon chain.

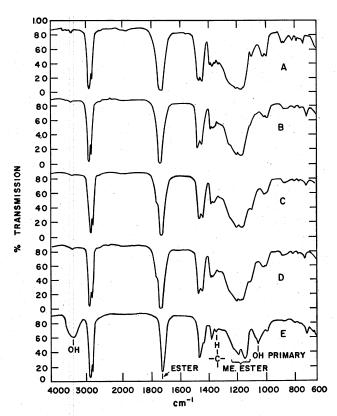


Fig. 1. Infrared spectra of (A) dimethyl ester of carboxy-hendecanoic acid, (B) dimethyl ester of carboxystearic acid, (C) methyl ester of carboxylated methyl ricinoleate, (D) methyl ester of carboxylated linoleic acid, and (E) methyl ester of carboxyoctadecanol.

The infrared spectrum of the methyl esters of carboxylated methyl ricinoleate (Figure 1, C) and of the methyl esters of carboxylated linoleic acid (Figure 1, D) are identical. These spectra are substantially the same as that of the dimethyl ester of carboxystearic acid (Figure 1, B) except for a weak band at 1765 cm.-1 This band definitely shows the presence of a new kind of carbonyl group, which is attributed to a lactone ring. This band is somewhat displaced from the 1790 cm.⁻¹ region for such known lactones as γ -stearolactone, γ -butyrolactone, and γ -valerolactone, but this might be expected from the difference of position of the lactone ring in the long chain. Also the size of the lactone ring its not known. Since the band at 1765 cm.-1 is rather weak, it suggests that only a part of the material is in the form of a lactone.

The infrared spectrum of the methyl esters of carboxyoctadecanol is shown in Figure 1, E. The methyl ester groups appear at 1725 cm.⁻¹ and as a triplet in the 1200 cm.⁻¹ region. Primary hydroxyl groups appear at 3400 cm.⁻¹ and at 1050 cm.⁻¹ Evidence for the branched carboxyl group appears at 1350 cm.⁻¹

More detailed spectra which confirm side-chain carboxylation are shown in Figures 2, 3, and 4. Figure 2 shows the 1300–1400 cm.-1 region of octadecanol (solid line) and of the methyl ester of carboxyoctadecanol (dotted line). (Concentrations are approximately 49 g. per liter in carbon tetrachloride.) An increase in the amount of absorption at approximately 1380 cm.-1 indicates additional CH₃ groups

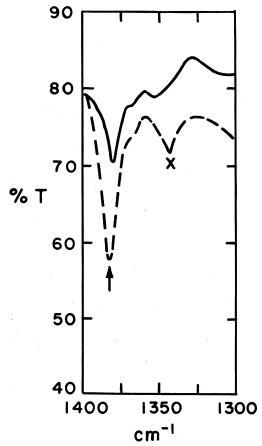


Fig. 2. Sections of infrared spectra of octadecanol (solid line) and methyl ester of carboxyoctadecanol (dotted line).

(from $-C-O-CH_3$). A weak band at approximately $\begin{array}{c|c} & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$

U−U−UH3 group) ∥

Figure 3 shows the 1300–1400 cm.-1 region of methyl stearate (solid line) and of the dimethyl ester of carboxystearic acid (dotted line). (Concentrations are approximately 49 g. per liter in carbon tetrachloride.) The tertiary hydrogen band (marked with an X) is weak and shows up merely as a shoulder. The –OCH₃ group of branched esters (marked with an arrow) seems to absorb at the same frequency as a normal C–CH₃ group, as seen in Figure 2.

In Figure 4 the carbonyl band of methyl stearate is shown as a solid line and of the dimethyl ester of carboxystearic acid as a dotted line. (Concentrations are approximately 10 g. per liter in carbon tetrachloride.) The calculated molar absorptivity for methyl stearate is 495, and for the dimethyl ester of carboxystearic acid it is 771, showing that the carboxylated compound has significant additional carbonyl. The fact that the molar absorptivity of the dimethyl ester of carboxystearic acid is less than two times the molar absorptivity of methyl stearate might be interpreted to mean that chain carboxylation is incomplete. The molar absorptivity of ester groups in different positions however is not necessarily the

same. Chemical analysis of carboxystearic acid and of its dimethyl ester shows that chain carboxylation is complete, bearing out the tentative conclusion that the molar absorptivity of the ester group on the chain is not the same as for a terminal ester group.

Reaction Mechanisms. Any reaction mechanisms proposed must account for the importance of the concentration of sulfuric acid, the role of water, the formation of isomeric products, and the apparent identity of certain products from carboxylated methyl ricinoleate and linoleic acid.

The need for concentrated sulfuric acid strongly suggests that intermediate carbonium ions are formed. Water is essential as a nucleophile to terminate the reaction and to permit the formation of a carboxyl group.

Carbon monoxide is a resonance hybrid of three contributing forms (9):

$$\ddot{\mathbf{C}} = \ddot{\mathbf{O}} : \longleftrightarrow \ddot{\mathbf{C}}^{+} - \ddot{\mathbf{O}} : \longleftrightarrow \ddot{\mathbf{C}} \equiv \mathbf{O}^{+}$$

The bond energy of carbon monoxide, 210 kcals./mole, is the greatest for any diatomic molecule, and it is attributable to the considerable resonance among the three canonical forms. The dipole moment of carbon monoxide is very small, indicating an approximately equal contribution of the two ionic forms shown.

It is reasonable to assume then that, in concentrated sulfuric acid, the double bond of the unsaturated compound is protonated to form a carbonium

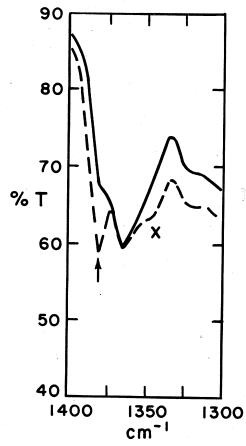


Fig. 3. Sections of infrared spectra of methyl stearate (solid line) and dimethyl ester of carboxystearic acid (dotted line).

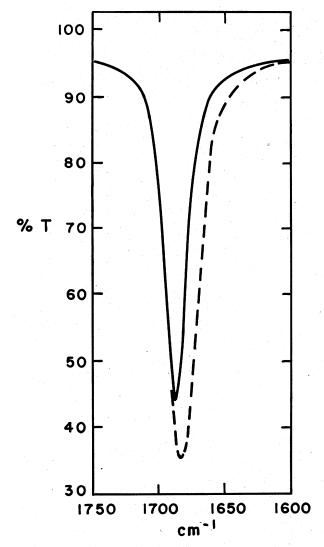


Fig. 4. Sections of infrared spectra of methyl stearate (solid line) and dimethyl ester of carboxystearic acid (dotted line).

ion (I), which on reaction with carbon monoxide forms an oxocarbonium ion (II) that is itself a resonance hybrid (IIa \longleftrightarrow IIb), as shown:

$$-CH = CH - + H_2SO_4 \longrightarrow -CH_2 - CH - + HSO_4$$

$$-CH_2 - CH - + C \equiv O^+ \longrightarrow$$

$$-CH_2 - CH - \longleftarrow -CH_2 - CH -$$

$$C \qquad C^+$$

$$||||$$

$$|||$$

IIb would be expected to react with a nucleophile, which in this case is water.

(IIb)

The above path accounts simply and directly for the products obtained from oleic acid, 10-hendecenoic acid, and oleyl alcohol. The carbonium ion mechanism also explains the formation of isomers and accounts for the changes in ring size and the branching noted by Koch (1). It also furnishes a logical explanation for the greater facility of carboxylation of branched alkenes and alcohols over corresponding straight-chain substances with carbon monoxide in sulfuric acid (1).

The proposed mechanism readily explains the identity of the carboxylated products from methyl ricinoleate and linoleic acid. In the former case a possible intermediate corresponding to IIb above is shown (central portion of one isomer only):

$$-\mathrm{CH} - \mathrm{CH}_2 - \mathrm{CH} - \\ \mathrm{OH} \qquad \qquad \begin{array}{c} \mathrm{C}^+ \\ \mathrm{O} \end{array}$$

Internal nucleophilic attack by the hydroxyl would produce a lactone:

$$\begin{array}{c|c} -\mathrm{CH} - \mathrm{CH_2} - \mathrm{CH} - + \mathrm{H} \\ | & | \\ \mathrm{O} - - - \mathrm{C} \\ | | \\ \mathrm{O} \end{array}$$

An alternative reasonable explanation, already mentioned, is that the hydroxycarboxylic acid actually forms and is then dehydrated in concentrated sulfuric acid. Another is that the ricinoleic moiety is first dehydrated to produce a dienoic acid, which then reacts as illustrated below, but we consider this unlikely.

With linoleic acid an intermediate corresponding to IIb is shown below:

Reaction of this ion with water forms the unsaturated carboxylic acid present in the crude product, as discussed earlier. The carboxyl group which has been introduced could then react by internal nucleophilic attack with the other double bond which has been converted to a carbonium ion:

$$-CH_2 - CH - CH_2 - CH - CH_2 - CH_$$

Acknowledgment

The authors wish to thank Miss Malena Der Avedisian for laboratory assistance; S. F. Herb for GLC determinations; C. R. Eddy, H. Susi, C. Leander, and Mrs. Anne S. Jahn for assistance in carrying out and interpreting spectra; and the Misses L. Scroggins and O. Panasiuk for carbon and hydrogen analyses.

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[Received April 28, 1960]